320
6-9-81
(88)

(2)

Dr. 2724

MASTER

SERI/PR-9062-1-T5

**Zn₃P₂ AS AN IMPROVED SEMICONDUCTOR FOR PHOTOVOLTAIC
SOLAR CELLS**

Ninth Quarterly Report for September 1—November 31, 1980

By
M. Bhushan
A. Catalano
P. S. Nayar

Dist-189
NTIS-22

Work Performed Under Contract No. AC02-76CH00178

Institute of Energy Conversion
University of Delaware
Newark, Delaware

U.S. Department of Energy

Solar Energy

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

DISCLAIMER

"This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof."

This report has been reproduced directly from the best available copy.

Available from the National Technical Information Service, U. S. Department of Commerce, Springfield, Virginia 22161.

Price: Printed Copy A04
Microfiche A01

Zn_3P_2 AS AN IMPROVED SEMICONDUCTOR FOR
PHOTOVOLTAIC SOLAR CELLS

NINTH QUARTERLY REPORT

September 1, 1980-November 31, 1980

Work Performed Under Department of Energy/Solar Energy Research
Institute Subcontract XR-9-8062-1

Institute of Energy Conversion
University of Delaware
Newark, Delaware 19711

ACKNOWLEDGEMENTS

This report was written by Dr. M. Bhushan, Dr. A. Catalano, and Dr. P. S. Nayar. During this time period Dr. M. Bhushan, Dr. P. S. Nayar, Dr. A. Catalano, Mr. L. DiNetta, Mr. R. Dozier, Mr. B. McCandless, Mr. P. Lasswell, Mr. J. Cambridge and Mr. W. Denny made contributions to the work discussed herein. The authors are grateful to Ms. D. Tortella and Mrs. T. Peterson for typing and compiling the report and to Ms. J. Joos for preparing the figures.

SUMMARY

Frequency and voltage dependent capacitance measurements of ZnO/Zn₃P₂ heterojunctions have been made and the results interpreted according to a model which considers the total capacitance arising from contributions due to the depletion layer capacitance, interface charges and a dipole charge. The capacitance of the devices is anomalously high at low frequencies but agrees well with the value calculated from the bulk carrier density at 1 MHz. The data suggests a significant contribution to the capacitance from the charging and discharging of interface states. A value of $V_D = 0.8$ eV is found at 1 MHz from $1/C^2$ vs V data, in good agreement with a simple band model of the heterojunction.

Direct evidence for a relationship between defects in the Zn₃P₂ (grain boundaries, dislocations etc.,) and the collected current have been found by comparing EBIC images of ZnO/Zn₃P₂ devices with the etched surfaces of the samples. Significant grain boundary effects are noted.

The series resistance of thin film Zn₃P₂ devices has been analyzed and the origin of the series resistance considered. Measurement of the carrier concentrations of the front and rear surfaces of the film are in the 10^{16} cm⁻³ range for films grown on Fe/C indicating that the bulk resistivity of the film is not excessive. An excessive sheet resistance of the conducting substrate film is indicated. Thin (≤ 10 μ m) films appear to undergo less reaction and usually result in a lower series resistance.

A new substrate consisting of sequentially deposited layers of Fe and Si on mica have resulted in improved device performance. These devices show a

generally lower R_s and ($< 10 \Omega\text{-cm}^2$) and higher V_{oc} , (in the 0.44-0.47 V range) compared to Fe/C coated substrates. Devices with a conversion efficiency as high as 2.7% have been obtained. Fill factors in excess of 50% have been obtained for the first time.

The diffusion coefficient of magnesium has been measured at 100°C and 125°C using a spectral response method. $D = 2 \pm .5 \cdot 10^{-11} \text{ cm}^2/\text{sec}$ at 100°C while $D = 5.0 \cdot 10^{-11} \text{ cm}^2/\text{sec}$ at 125°C.

A model including contributions from both diffusion and space charge recombination terms was utilized to calculate the open circuit voltage and short circuit current as a function of junction depth of the n on p devices. This model predicts a maximum $V_{oc} = 0.98 \text{ V}$ for an n-layer thickness of $\sim 1 \mu\text{m}$.

A comparison of the experimental J_{sc} and V_{oc} as a function of junction depth was made by characterizing the devices after successive surface diffusions. The qualitative features predicted by theory were realized experimentally; however, the V_{oc} was much lower than expected. The difference is believed to be due to an incorrect value of electron mobility or lifetime, or alternatively incomplete ionization of the donor impurities.

TABLE OF CONTENTS

	PAGE
ACKNOWLEDGEMENTS -----	1
SUMMARY -----	2
A. ZnO/Zn ₃ P ₂ Heterojunction Devices -----	5
1. Introduction -----	"
2. Capacitance Measurements of ZnO/Zn ₃ P ₂ Heterojunction -----	"
3. EBIC Examination of ZnO/Zn ₃ P ₂ Devices -----	15
B. Thin Film Zn ₃ P ₂ Devices -----	22
1. Introduction -----	"
2. Series Resistance of the Thin Film Device -----	"
3. Mica/Fe/Si Substrates -----	26
C. p-n Homojunction Device Development -----	32
1. Introduction -----	"
2. Theoretical Model of a p/n Homojunction -----	"
3. Measurement of the Diffusion Coefficient of Mg in Zn ₃ P ₂ -----	36
4. Performance of p/n Homojunction Devices -----	42
Appendix -----	55

A. ZnO/Zn₃P₂ Heterojunction Devices

A.1 Introduction

The results of our previous investigations of Zn₃P₂ heterojunctions revealed that the best devices achieved a V_{OC} of ~0.4 volt and a conversion efficiency uncorrected for loss of about 2%. Photocurrent suppression via interface states was indicated by the non linear dependence of log J_{SC} vs V_{OC} in these devices. Since the interface states play a significant role in determining the equilibrium band diagram and the electrical properties of the heterojunction, some studies of the Zn₃P₂/ZnO interface were carried out to estimate the interface state density and related parameters. Since the capacitance of the junction is a function of these states when present, capacitance measurements as a function of frequency are employed to study these states.

A.2 Capacitance Measurements of ZnO/Zn₃P₂ Heterojunctions

The capacitance of an ideal p-n heterojunction in the absence of interface states is essentially the same as that of a p-n homojunction except that the abrupt change in dielectric constant across the junction has to be considered. Under these conditions, the capacitance per unit area of a p-n heterojunction is given by

$$C = \left[\frac{q \epsilon_1 \epsilon_2 N_1 N_2}{2(\epsilon_1 N_1 + \epsilon_2 N_2)} \right]^{1/2} (V_D - V)^{-1/2} \quad \text{A.2-1}$$

where ϵ is the dielectric constant, N is the carrier concentration with subscripts 1 and 2 corresponding to p and n-type semiconductors, respectively, V is the bias voltage and V_D is the diffusion voltage. For the specific case of the Zn₃P₂/ZnO heterojunction $\epsilon_1 = 11$, $\epsilon_2 = 8.2$, $N_1 = 10^{15} \text{ cm}^{-3}$ and $N_2 = 10^{17} \text{ cm}^{-3}$. Thus for a diffusion voltage of 1.0V, the calculated capacitance per unit area under zero bias is 8.8 nf/cm².

Experimentally the low frequency capacitance of our $\text{Zn}_3\text{P}_2/\text{ZnO}$ diodes prepared with $N_1 \approx 10^{15} \text{ cm}^{-3}$ and $N_2 \approx 10^{17} \text{ cm}^{-3}$ were always found to be much larger than the theoretical value. The high frequency (1MHZ) capacitance, however, is close to the predicted value. The discrepancy can be explained if we take into account the contribution to the capacitance by interface states.

Methods have been developed to study the surface states in MOS structures. The heterojunction case is more difficult to analyze on the basis of a MOS model for the following reasons. The heterojunction contains a voltage dependent capacitance on both sides of the junction, while an MOS structure contains one constant capacitance due to an oxide layer and one voltage dependent capacitance. Under bias no current flows in a MOS structure and hence a constant quasi-Fermi level exists across the semiconductor which determines the filling and emptying of the interface states at a given bias. In a heterojunction, however, a current flows when the bias is applied and the filling and emptying of interface states cannot be predicted.

While calculating the total capacitance of a $\text{Zn}_3\text{P}_2/\text{ZnO}$ heterojunction, the possible effects of electric dipoles caused by the result of two sets of interface states, one in each semiconductor forming the junction, is also taken into account. Since the interface states in a heterojunction cannot be related to any distinct Fermi level, the differential change in net charge on the interface is written by $(\frac{dQ_s}{dV})$ where Q_s is the interface charge and the variation in electric dipole (ϕ) is written as $\frac{d\phi}{dV}$.

The total capacitance of the junction will be due to the combined effects of depletion layer capacitance, interface charge and the possible dipole charge. The equivalent circuit for such a model is given in Figure A.2-1. Since each state has its own emptying and filling rates and has different relaxation

- R_P - Shunt Resistance
- R_S - Series Bulk Resistance
- C_{IS} - Interface Charge Capacitance
- C_ϕ - Dipole Capacitance
- C_D - Depletion Layer Capacitance

FIGURE A:2-1: Equivalent circuit used in the analysis of the capacitance of ZnO/Zn₃P₂ heterojunctions.

times, the total capacitance of the junction including frequency effects can be represented by equation A.2-2.

$$C = B_1 (V_D - V - \phi - B_2 Q_s^2)^{-1/2} \times \left[1 + \frac{f(V)}{1 + (\omega t)^2} \frac{d Q_s}{d V} + \frac{1}{1 + (\omega t)^2} \frac{d \phi}{d V} \right] \quad A.2-2$$

where

$$B_1 = \left[\frac{q \epsilon_1 \epsilon_2 N_1 N_2}{2(\epsilon_1 N_1 + \epsilon_2 N_2)} \right]^{1/2} \quad A.2-3$$

$$B_2 = \frac{1}{2 q (\epsilon_1 N_1 + \epsilon_2 N_2)} \quad A.2-4$$

and

$$f(V) = -2 B_2 Q_s^2 - 2 \left(\frac{\epsilon_1 N_1}{\epsilon_2 N_2} \right)^{1/2} B_2^{1/2} (V_D - V - \phi - B_2 Q_s^2) \quad A.2-5$$

At frequencies high enough such that $(\omega t)^2 \gg 1$, equation A.2-2 can be approximated to

$$C \approx B_1 (V_D - V - \phi - B_2 Q_s^2)^{-1/2} \quad A.2-6$$

The room temperature dark capacitance was measured as a function of frequency using an HP 4274A multifrequency LCR meter at an oscillator voltage of 10 mV rms. The ZnO/Zn₃P₂ device was prepared by r.f. sputtering the ZnO onto a Zn₃P₂ surface which had been sputter etched for 15 seconds. The results are presented in Figure A.2-2. At very low frequencies (100 - 400 HZ) the capacitance is nearly constant. At higher frequencies the capacitance decreases, indicating that the charging and discharging of interface states cannot follow the applied signal. An increase in conductance occurs above about 40 KHZ. The admittance components as a function of frequency are shown in Figure A.2-3. Both conductance and susceptance vary with frequency. However, the conductance change is small up to a frequency of ~ 40 KHZ. A crossover frequency is evident below which the conductance is nearly frequency independent.

FIGURE A.2-2: Conductance and capacitance of ZnO/Zn₃P₂ heterojunctions as a function of frequency.

The maximum diffusion voltage of $\text{Zn}_3\text{P}_2/\text{ZnO}$ heterojunctions can be estimated using the band gap (E_g) and electron affinities (χ) of Zn_3P_2 and ZnO . For Zn_3P_2 , $\chi_p = 3.8$ eV and for ZnO , $\chi_n = 4.2$ eV. The conduction band discontinuity therefore, is $\Delta E_c = 0.4$ eV. Assuming a hole effective mass in Zn_3P_2 equal to that of free electron and an acceptor concentration of $2 \times 10^{15} \text{ cm}^{-3}$, the Fermi level in Zn_3P_2 is located at 0.24 eV from the top of the valence band. For ZnO , $m_e^* = 0.24 m_0$ so that for $N_D = 5 \times 10^{17} \text{ cm}^{-3}$, the Fermi level is ~ 0.05 eV below the conduction band. Thus a diffusion voltage of ~ 0.8 volt results.

The diffusion voltage for $\text{Zn}_3\text{P}_2/\text{ZnO}$ heterojunction can be determined from the high frequency capacitance data where interface effects are negligible and the junction capacitance is mainly due to the depletion layer capacitance. Figure A.2-4 shows the $1/C^2$ plot as a function of reverse bias at various frequencies. These measurements suggest a high density of interface states. At frequencies higher than 40 KHZ, the junction exhibits characteristics in which $1/C^2$ is nearly a linear function applied bias. However, a decrease in slope with increase in reverse bias is observed. The apparent diffusion voltage V_{Di} can be estimated by extrapolating $1/C^2$ at low reverse bias to zero and using equation A.2-6 so that

$$V_{Di} = V_D - \phi - \frac{Q_s^2}{2 q (\epsilon_1 N_1 + \epsilon_2 N_2)} \quad \text{A.2-7}$$

Neglecting the last two terms in A.2-7 and assuming V_{Di} is the actual diffusion voltage, the data at 100 KHZ gives $V_D = 0.8$ volt which is in fairly good agreement with the theoretical value.

The capacitance data at 40 KHZ gives an apparent diffusion voltage of ~ 0.06 V. It is noteworthy that the curves at 100 KHZ and 40 KHZ, at low reverse

FIGURE A.2-4: $1/C^2$ vs V of $\text{ZnO}/\text{Zn}_3\text{P}_2$ diodes for frequencies between $10^4 - 10^2\text{Hz}$

bias have nearly the same slope and yield an acceptor concentration of $\sim 1.5 \times 10^{15} \text{ cm}^{-3}$ in good agreement with the acceptor concentration of Zn_3P_2 calculated from the resistivity value. This data, therefore, indicates that the two interface terms ϕ and Q_s must play significant roles. If ZnO is considered to be heavily doped ($\sim 5 \times 10^{17}$ or larger) most of the field exists in Zn_3P_2 . Therefore, as a first approximation the effect of dipoles (ϕ) may be neglected. Assuming a conduction band edge discontinuity of 0.4 eV, the number of minimum charged interface states (N_s) necessary to account the apparent diffusion voltage can be calculated. Using the 40 KHZ data yields, $N_s = 9.6 \times 10^{11} \text{ cm}^{-2}$. From these studies, it is likely that in $\text{Zn}_3\text{P}_2/\text{ZnO}$ heterojunctions the interface states are dense enough to have an appreciable effect on the band bending and consequent electrical characteristics of the $\text{Zn}_3\text{P}_2/\text{ZnO}$ heterojunction. The photocapacitance at low light illumination (Figure A.2-5) seems to support this model. The high density of interface states can be attributed to the large lattice mismatch for ZnO and Zn_3P_2 . Initial thermally stimulated studies of $\text{Zn}_3\text{P}_2/\text{ZnO}$ junctions reveal that these states arise from deep levels with very complex spectral characteristics. Further investigations are expected to yield more information about these states and their interaction with the photogenerated carriers.

FIGURE A.2-5: Photocapacitance at low intensive as a function of frequency
for ZnO/Zn₃P₂ diode.

A.3 EBIC Examination of ZnO/Zn₃P₂ Devices

During the last quarter we used EBIC measurements to assess non uniformities in the response of ZnO/Zn₃P₂ heterojunctions. Those results showed evidence of grain boundary effects on the collected current.

During this quarter we have established a one-to-one correspondence between defects in the Zn₃P₂ and the current measured by the EBIC method. ZnO devices were fabricated by r.f. sputtering onto the sputter etched, polycrystalline Zn₃P₂ surface. The devices were examined in the EBIC mode in a Phillips 401 SEM using accelerating voltages between 15 - 30 keV. Higher voltages reduced EBIC resolution because of the increased range of the electron beam. An acceleration voltage below 15 keV gave extremely low signals because significant electron beam absorption occurred in the ZnO top layer. After EBIC imaging, a fiduciary mark was placed on the surface of the sample so its orientation could be preserved, and the ZnO stripped off in concentrated NaOH.

Grain boundaries and dislocations were disclosed by etching the Zn₃P₂ in an aqueous solution consisting of 8 grams KI and 2 grams iodine dissolved in 400 ml of deionized water. Immersion for 24 hours at 25°C was sufficient to develop the sample.

Figures A.3 - 1 to 3 show features typical of the etched samples.

Figure A.3-1 shows a grain boundary disclosed by etching. A line of dislocations can be seen to cross the grain boundary at right angles. The geometry of the dislocation etch pit is clearly evident at higher magnification in Figure A.3-2. The etchant apparently attacks crystal faces at different rates and produces a texture related to the orientation as shown in Figure A.3-3 in which two grains

FIGURE A.3-1: Zn_3P_2 sample etched for 24 hours in $\text{KI} + \text{I}_2$ etch. Photo shows grain boundary crossed by a line of dislocations.

FIGURE A.3-2: SEM photograph showing geometry of etch pit (5000X).

FIGURE A.3-3: SEM photograph (3000X) of KI + I₂ etched sample showing different textures in each grain.

are pictured. A quantitative relationship between crystal orientation and texture is planned for the next quarter, and may serve as a useful quick method for determining crystal orientation.

Nonuniformities in device response in the EBIC mode translate directly into material defects extant in the Zn_3P_2 as shown in Figure A.3-4 a,b which compare the EBIC (Figure A.3-4a) with the etched (Figure A.3-4b) sample. The three major grains show a device response which differ by a factor of 3. Also noteworthy is a line scan of the electron beam induced current which shows a sharp current increase at the grain boundary (bright line). In contrast, intra-grain and grain boundaries at the top right of the photo are low and suggest either a lower diffusion length or the dominance of some minority carrier recombination mechanism at the interface. It should be noted that the highest current and voltage are obtained with in situ sputter etch time of 15 seconds prior to ZnO deposition, which we believe removes the native oxide and enables an intimate ZnO - Zn_3P_2 contact. Since this oxide thickness may depend on crystallite orientation, the different output between grains may reflect incomplete oxide removal within those grains. The origin of the different current collection efficiencies at grain boundaries is unknown; however, I-V measurements between grains which show enhanced output do not exhibit non-linear I-V traces down to 273°K.

These results show a marked effect of grain boundaries, defects and possibly grain orientation on current output of the $\text{ZnO}/\text{Zn}_3\text{P}_2$ devices. It thus appears that an unambiguous examination of the $\text{ZnO}/\text{Zn}_3\text{P}_2$ heterojunction requires the use of relatively perfect, oriented single crystals. During the next quarter we will attempt to prepare such samples for further device

NOV 20 1990

FIGURE A.3-4a: EBIC photograph (Z-modulated) of $\text{ZnO}/\text{Zn}_3\text{P}_2$ device prior to etching to disclose grain

FIGURE A.3-4b: Micrograph of same region after etching.
Note corresponding features.

preparation and analysis, begin work quantifying the observed material defects disclosed by etching (via TEM) and start to establish a relationship between device output and these defects.

B. Thin Film Zn₃P₂ Devices

B.1 Introduction

Large area (~1 cm²) TMF (Mg/Zn₃P₂) devices on thin Zn₃P₂ films, grown on mica/Fe/C and silicon steel substrates, with total area conversion efficiencies of ~2.5% have been reported previously. The device performance is limited by the low fill factor (< 50%) in both cases. The devices on Mica/Fe/C substrates have high series resistance, R_S, and low J_{SC} whereas the devices on silicon steel have low V_{OC} and shunt resistance, R_{SH}.

High substrate temperature (~580°C,) during film growth by close-space transport, restricts the choice of substrates. Appendix A lists all the substrates that have been used since January 1980. Of these, Mica/Fe/C and silicon (or stainless) steel have proved to be the most promising.

During this quarter, development of TMF devices on Mica/Fe/C substrates was continued towards the goal of reducing the series resistance. In addition, a new substrate, mica with evaporated layers of Fe and Si, was developed.

B.2 Series Resistance of the Thin Film Device.

The series resistance, R_S, is calculated for the device configuration shown in Figure B.2-1. The contribution to R_S comes from; a) the thin Mg film, b) the Zn₃P₂ film, and c) the ohmic contact at the back. R_S for a 1 cm x 1 cm device is given by

$$R_S = \rho_Z d_Z + \frac{0.5}{3} \frac{\rho_m}{t_m} + 2 \times 10^{-2} \frac{\rho_s}{t_s} + \frac{\rho_s}{t_s} \times \frac{1}{4}$$

SCHEMATIC DIAGRAM OF THIN Zn_3P_2 FILM DEVICE

TOP VIEW

CROSS-SECTIONAL VIEW

FIGURE B.2-1: Device configuration used series resistance calculation.

IEC81048

where ρ_z = Zn_3P_2 film resistivity

d_z = Zn_3P_2 film thickness

$\frac{\rho_m}{t_m}$ = sheet resistivity of thin Mg film

$\frac{\rho_s}{t_s}$ = sheet resistivity of the substrate

l = distance between the device edge and Ag electrode.

Commonly these variables have the following values:

$$\rho_z = 500 \Omega\text{-cm}, d_z = 10^{-3} \text{ cm}, \frac{\rho_m}{t_m} = 20 \Omega/\square.$$

$$\frac{\rho_s}{t_s} = 5 \Omega/\square \text{ and } l = 0.2 \text{ cm}, R_s = 4.15 \Omega\text{-cm}^2.$$

TMF devices on Mica/Fe/C substrates have $R_s > 10 \Omega\text{cm}^2$. Table B.2-I below lists the cell parameters for some devices prepared during this quarter. All devices were 0.5 cm^2 ($1 \text{ cm} \times 0.5 \text{ cm}$) in area. The cells were illuminated by an ELH lamp at an intensity of 87.5 mW/cm^2 . The carrier concentration of the film was determined from the capacitance at zero voltage bias. The diode factor, A , and reverse saturation current, J_0 , were determined from a plot of $\log J_{sc}$ vs V_{oc} .

Table B.2-I

Sample #	J_{sc} (mA/cm ²)	V_{oc} (Volts)	FF	η (%) Total (area)	$R_s \times A$ ($\Omega\text{-cm}^2$)	N_D (cm ⁻³)	A	J_0 (Amp/cm ²)
EPI-1185	11.80	0.438	0.40	2.36	10	1.58×10^{16}	1.78	9.93×10^{-7}
EPI-1190	11.50	0.437	0.35	2.01	14	1.63×10^{16}	1.72	7.23×10^{-7}
EPI-1195	10.80	0.398	0.43	2.10	7.5	2.32×10^{16}	1.37	1.61×10^{-7}
EPI-1219	7.92	0.411	0.32	1.18	35	7.07×10^{15}	1.49	1.62×10^{-7}
EPI-1217	7.82	0.430	0.33	1.23	35	9.58×10^{15}	1.61	2.27×10^{-7}

Laser scans of these devices showed that the cell response did not fall away from the contact to the thin Mg film. Since the carrier concentration in the Zn_3P_2 films near the junction is high ($\sim 10^{16} \text{ cm}^{-3}$, corresponding to $\rho_z = 30 \Omega\text{-cm}$), the Mg and Zn_3P_2 films should not cause a high R_s . Earlier it had been speculated that Fe from the substrate acted as a compensating impurity, lowering the carrier concentration in Zn_3P_2 film near the substrate. To check this, thin Zn_3P_2 films grown under identical conditions on Mica/Fe/C were removed from the substrate by dissolving the iron layer in dilute HCl. Ag was evaporated on the front surface and 1 mm diameter Mg dots were evaporated on what was formerly the back surface. The carrier concentration, N_p , was determined from the capacitance at zero bias. Table B.2-II gives N_p on both the front and back surfaces for films prepared on the same substrates. The capacitance measurements were performed at 100 HZ using a Hewlett Packard LCR Meter, Model #4274A.

TABLE B.2-II

Substrate #50			Mica/Fe(600Å)/C (700Å)		
Front Surface			Back Surface		
Sample #	$R_s \times A$ ($\Omega\text{-cm}^2$)	N_p (cm^{-3})	Sample #	$R_s \times A$ ($\Omega\text{-cm}^2$)	N_p (cm^{-3})
EPI-1277	8.33	1.3×10^{16}	EPI-1284	7.8	2.58×10^{17}
EPI-1280	25.0	4.7×10^{16}	EPI-1289	11.1	1.17×10^{17}
Substrate #52			Mica/Fe(600Å)/C(100Å)		
TPZ-27	312	9.14×10^{15}	EPI-1327	107	7.31×10^{16}

The carrier concentration in the Zn_3P_2 films is higher near the substrate by an order of magnitude. Earlier, films grown on silicon steel which were

doped with iron, also had $N_p \sim 10^{17} \text{ cm}^{-3}$. These results indicate that iron acts as a p-type dopant in Zn_3P_2 , raising the carrier concentration to $\sim 10^{17} \text{ cm}^{-3}$. This clearly demonstrates that the bulk resistivity of the film is not a major contributor to R_s of the device.

This data suggests that the contact resistance is not large; previous measurements of evaporated carbon on single crystals at the same approximate doping level showed a contact resistance comparable to silver. During the next quarter we plan to measure the contact resistance as well as the sheet resistance of the substrate.

It has been reported earlier that the series resistance in Schottky barrier grid devices ($0.5 \times 0.5 \text{ mm}$) was reduced considerably by increasing the carbon layer thickness from $500\text{\AA}$ to $1000\text{\AA}$. However, efforts to correlate R_s with carbon thickness on 1 cm^2 devices were not successful. A set of substrates was prepared with carbon thickness ranging from $600\text{\AA}$ to $1000\text{\AA}$. $\text{Mg}/\text{Zn}_3\text{P}_2$ diodes processed on these substrates had $R_s \times A$ in the range of 8 to $550 \Omega\text{-cm}^2$. Such wide variations in R_s depending on the substrate and film process conditions make the Mica/Fe/C substrate unsatisfactory.

B.3 Mica/Fe/Si Substrates

Since silicon has been a more effective diffusion barrier on silicon steel, mica with evaporated layers of Fe and Si was used as an alternative to Mica/Fe/C substrates. Successive layers of $500\text{\AA}$ to $1000\text{\AA}$ of Fe and $100\text{\AA}$ Si were e-beam evaporated on freshly cleaved mica. Si deposition was carried out at pressures below 5×10^{-7} Torr to prevent the formation of an oxide layer.

Si has an expansion coefficient of 4.5×10^{-6} , which is lower than that of Fe and Zn_3P_2 . The thickness of Si film is critical because excessive thermal

or intrinsic stress causes the Zn_3P_2 films to peel off the substrates when the Si thickness is greater than $150\text{\AA}$.

Thin Zn_3P_2 films grown on Mica/Fe/Si were uniform in appearance and the grain size was large ($\geq 5 \mu\text{m}$). TMF Mg/ Zn_3P_2 diodes were prepared. Due to partial breakdown of the sputtering equipment, the Zn_3P_2 surface could not be sputter etched prior to Mg deposition. This results in a higher ratio of sheet resistance of optical transmission compared to sputter etched surfaces and unoptimized device performance.

TABLE B.3-I

TMF Devices on Mica/Fe/Si Substrates

Sample #	Area (cm^2)	J_{sc} (mA/cm^2)	V_{oc} (Volts)	FF	(%) (Total Area)	$R_s \times A$ ($\Omega\text{-cm}^2$)	N_{D} (cm^{-3})	A	J_0 (Amp/cm^2)
TPZ-35	0.5	9.44	0.465	0.44	2.21	3.5	----	1.85	5.75×10^{-7}
TPZ-42	0.5	11.48	0.443	0.42	2.44	2.0	4.8×10^{15}	1.27	1.7×10^{-8}
TPZ-49	0.5	12.46	0.457	0.41	2.67	4.5	1.72×10^{16}	1.89	9.6×10^{-7}
TPZ-52	0.125	12.0	0.380	0.52	2.71	3.0	1.95×10^{16}	1.43	3.5×10^{-7}
TPZ-53	0.5	11.94	0.363	0.41	2.03	2.5	1.56×10^{16}	1.65	2.5×10^{-6}
EPI-925 (on Mica/ Fe/C)	1.0	11.3	0.452	0.47	2.74	8.0	----	----	----

Prior experience has shown that sputter etching the Zn_3P_2 surface before Mg deposition produces a marked improvement in J_{sc} (via increased optical transmission) and the diode characteristics (high R_{sh}) and a higher V_{oc} . Despite the present difficulties in processing, the devices on Mica/Fe/Si substrates are comparable in total area conversion efficiency to those produced earlier on Fe/C and 3% Si-Fe substrates. Table B.3-I lists the cell parameters of 5 devices out of a total of 20 processed so far. For comparison, the parameters of the best device (EPI-925) produced so far on Mica/Fe/C are also listed.

Devices prepared on Mica/Fe/Si develop a maximum total area J_{SC} of $\sim 12 \text{ mA/cm}^2$ despite the poor optical transmission of the TMF. The films generally exhibit a diffusion length of $4 \mu\text{m}$ which is near the maximum found for thin Zn_3P_2 films. This is deduced from the spectral dependence of the collection efficiency at long wavelengths.

The series resistance $R_s \times A$, for the large area (0.5 cm^2) devices on mica is $< 5 \Omega\text{-cm}^2$ for the first time. The carrier concentration of the films, deduced from the zero bias capacitance is of the order of 10^{16} cm^{-3} , comparable to films grown on Fe/C coated mica. The lower overall resistance of the present device is attributed to an improved contact or sheet resistance. The high contact resistance at the back is believed due to a chemical interaction of the contact and semiconductor elements. For example, films grown on Fe/Si substrates show an anomalously large rate of increase in series resistance with film thickness. Auger profiles of the back contact will be performed during the next quarter to answer this question more definitively.

The open circuit voltage of devices prepared on Fe/Si devices is improved over all previous thin-film cells. For example, $V_{OC} = .465 \text{ volts}$ has been obtained at 26°C and V_{OC} 's are routinely obtained in the 0.45V range, in contrast to Fe/C substrate devices. V_{OC} is larger in part due to the higher shunt resistance in the device and the lower J_0 arising from carrier concentrations in the range of $5 \cdot 10^{15} \text{ cm}^{-3}$. Table B.3-II compares the device parameters of several samples. The devices exhibit an extremely uniform response as shown in the laser scan of Figure B.3-2.

Since the series resistance of the device is markedly lowered by reducing the thickness of the Zn_3P_2 film, it is worthwhile to model the effect of thickness

FIGURE B.3-2: Laser scan of a $\text{Mg/Zn}_3\text{P}_2$ device on Mica/Fe/Si substrate.

on short circuit current. Figure B.3-3 plots the calculated maximum current output of a device, ignoring reflection losses and ignoring collection by the field at the junction. It can readily be seen that for a 5 μm diffusion length, a film thickness in excess of 2 μm results in little improvement in current.

TABLE B.3-II

Sample #	Film growth Conditions		Film Thickness (μm)	J _{sc} (mA/cm ²)	V _{oc} (Volts)	FF (%)	R _s x A (Ω-cm ²)	N _p (cm ⁻³)	
	Source temp(°C)	Growth time (Min)							
TPZ-42	675	13	7	11.48	0.443	0.42	2.44	2.0	4.87 x 10 ¹⁵
TPZ-43	675	15	15	6.2	0.455	0.27	0.87	47.5	4.63 x 10 ¹⁵
TPZ-44	675	20	20	3.7	0.457	0.28	0.54	90.0	---

FIGURE B.3-3: Calculated J_{sc} of device a function of film thickness;
 $L_n = 5 \mu\text{m}$ assumed in the calculations.

C. p-n HOMOJUNCTION DEVICE DEVELOPMENT

C.1 Introduction

Zn_3P_2 has been reported to exhibit only p-type conductivity at room temperature, with phosphorus interstitials acting as acceptor states. Recently, some evidence of n-type Zn_3P_2 has been found when $\text{Mg}/\text{Zn}_3\text{P}_2$ (p-type) Schottky diodes were heated at temperatures above 750°C . The formation of a p-n junction as a result of this heat treatment is supported by three observations:

- a) EBIC scans of a cross-section show that the peak response moves away from the $\text{Mg}/\text{Zn}_3\text{P}_2$ contact with increasing heating time.
- b) Spectral response measurements of transparent $\text{Mg}/\text{Zn}_3\text{P}_2$ devices show that the peak collection efficiency shifts towards longer wavelengths indicating a buried junction.
- c) V_{oc} increases from < 0.5 volts to 0.6 volts and the reverse saturation current, J_0 , decreases by at least an order of magnitude. The diffusion voltage, obtained for plots of J_0 vs $1/T$ increases to values $\sim E_g/2$.

C.2 Theoretical Model* of a p/n Homojunction

Theoretical calculations of J_{sc} and V_{oc} as a function of the junction depth, x_j were performed. J_{sc} was calculated by summing up the light generated

* Computer programs for theoretical modeling p-n homojunction Zn_3P_2 devices were developed by I. Pereyra and J. Felton under SERI subcontract DE-AC-1-79ET-23107.

current contributions from the n region J_{scn} , space charge region J_{scw} and the p region J_{scp} where

$$J_{scn} = q \phi(\lambda) \sum_{\alpha} \frac{\alpha L_p}{(\alpha^2 L_p^2 - 1)} \times \frac{\alpha L_p - \exp(-\alpha x) [\sinh(\frac{x}{L_p}) - \alpha L_p \cosh(\frac{x}{L_p})]}{\cosh(\frac{x}{L_p})} \quad (C.2-1)$$

$$J_{scw} = q \phi(\lambda) \sum_{\alpha} \exp(-\alpha x) [1 - \exp(-\alpha w)] \quad (C.2-3)$$

$$J_{scp} = q \phi(\lambda) \sum_{\alpha} \frac{\alpha L_n}{(\alpha^2 L_n^2 - 1)} \exp(-\alpha(x+w)) \times \frac{\alpha L_n \exp(-\alpha y) + \alpha L_n \cosh(y/L_n) - \sinh(y/L_n)}{\cosh(y/L_n)} \quad (C.2-3)$$

Here, L_n and L_p are the minority carrier diffusion lengths in the p and n regions, w is the width of the space-charge region, and x and y are the thickness of the n and p layers respectively. The surface-recombination velocity is taken as zero. The summation was carried over the AM-1.5 solar spectrum. The junction is assumed to be abrupt with the electron carrier concentration, $N_n = 1 \times 10^{17} \text{ cm}^{-3}$. Figure C.2-1 is a plot of J_{sc} vs thickness of the n layer with $N_p = 5 \times 10^{16} \text{ cm}^{-3}$ and $L_n = L_p = 3.5 \text{ } \mu\text{m}$. Initially, J_{sc} increases with x due to carrier collection from both layers and then starts to decrease for x greater than the absorption length $1/\alpha$.

In calculating V_{oc} , the contributions due to minority carrier diffusion and space-charge recombination were taken into account. The diode equation is

$$J = J_{od} \left[\exp\left(\frac{qV}{kT}\right) - 1 \right] + J_{on} \left[\exp\left(\frac{qV}{2kT}\right) - 1 \right] \quad (C.2-4)$$

FIGURE C.2-1: J_{sc} and V_{oc} n-on-p device calculated as a function of n-layer thickness.

where the first term is due to minority carrier diffusion and has a diode factor of 1.0 while the second term is due to space-charge recombination and has a diode factor of 2.0. J_{sc} is given by

$$J_{sc} = J_{od} \exp\left(\frac{qV_{oc}}{kT}\right) + J_{on} \exp\left(\frac{qV_{oc}}{2kT}\right) \quad (C.2-5)$$

this is a quadratic equation in $\exp\left(\frac{qV_{oc}}{2kT}\right)$ and therefore

$$V_{oc} = \frac{2kT}{q} L_n \left[\left(\frac{J_{on}}{2J_{od}}\right)^2 + \frac{J_{sc}}{J_{od}} \right]^{1/2} - \frac{J_{on}}{2J_{od}} \quad (C.2-6)$$

and $J_{on} = q N_i \frac{w}{\tau}$

$$J_{od} = q N_i^2 \left[\frac{D_n}{N_p L_n} + \frac{D_p}{N_n L_p \tanh\left(\frac{x}{L_p}\right)} \right] \quad (C.2-7)$$

where N_i is the intrinsic carrier concentration in Zn_3P_2 , D_n and D_p are the electron and hole diffusion coefficients and τ is the lifetime in the space charge region.

Also

$$D = \frac{kT}{q} \mu ; L = (\tau D)^{1/2} \quad (C.2-8a,b)$$

where μ is the mobility. The calculations are carried out at $T = 298$ K for and $L_n = L_p$, $\mu_n = \mu_p = 25 \text{ V}^{-1} \text{ cm}^2/\text{sec}$. $N_i = 3 \times 10^6 \text{ cm}^{-3}$ ($E_g = 1.5 \text{ eV}$) and $N_0 = 1 \times 10^{17} \text{ cm}^{-3}$

The theoretical values of open circuit voltage were obtained by substituting J_{on} and J_{od} in equation C.2-6 for a given junction depth, x . J_{sc} in equation C.2-6 was calculated from the steady state carrier generation - collection expressions C.2-1 to 3. Figure C.2-1 gives the results of the calculation as a plot of V_{oc} and J_{sc} vs junction depth. It can be readily seen that the maximum conversion efficiency occurs for a junction depth x of approximately $1 \mu\text{m}$ where $\eta \approx 17\%$.

C.3 Measurement of Diffusion Coefficient of Mg in Zn_3P_2

The diffusion coefficient of Mg in Zn_3P_2 was calculated from measurements of the collection efficiency of heated devices. The method was outlined in the last quarterly report. A thin, transparent film of Mg was deposited on polycrystalline Zn_3P_2 wafers by d.c. sputtering. The wafers were then heated in air at temperatures of 100°C and 125°C. The collection efficiency was measured as a function of wavelength after each heat treatment. The diffusion profile was assumed to be given by a complementary error function distribution. The diffusion coefficient, $D(T)$, at temperature T is given by

$$D(T) = \frac{x_j^2}{4t \operatorname{erfc} \left(1 - \frac{N_p}{N_0}\right)} \quad \text{C.3-1}$$

where x_j is the junction depth, t is the heat treatment time, N_p is the carrier concentration in p-type Zn_3P_2 and N_0 is the surface concentration of Mg atoms.

The surface concentration of Mg atoms is determined indirectly by heating Mg/ Zn_3P_2 Schottky devices on highly doped Zn_3P_2 wafers. When $N_p \geq N_0$, no evidence of Mg diffusion is observed; i.e., the spectral response of the device remains unchanged after prolonged heat treatment. So far, the experimental results show that N_0 at 100°C is $< 1.8 \times 10^{17} \text{ cm}^{-3}$ and $> 5.2 \times 10^{16} \text{ cm}^{-3}$. At 75°C and 125°C N_0 is $\leq 2 \times 10^{17} \text{ cm}^{-3}$. As N_0 is not strongly dependent on temperature, a value of $1 \times 10^{17} \text{ cm}^{-3}$ is assumed at 100°C and 125°C.

The base carrier concentration is determined from 1) resistivity of the wafer ($\mu_p = 20 \text{ V}^{-1} \text{ cm}^2/\text{sec}$); 2) the capacitance at zero voltage bias; and 3) the slope of $\frac{d(1/C^2)}{dV}$ vs voltage plot.

Figures C.3-1 to 3 show the log of collection efficiency as a function of the square root of time at wavelengths < 650 nm for three samples used in these measurements. The slope of this straight line is a measure of the junction depth as

$$\log \eta = \log \eta_0 - \frac{x_j}{L_p} \quad \text{C.3-2}$$

The diffusion length in the p-layer was determined from the spectral response of unheated devices. The collection efficiency is given by

$$\eta = T_m \frac{L_n}{\alpha L_n + 1} \quad \text{C.3-3}$$

where T_m is the fraction of incident light reaching the junction. By plotting $T_m \eta^{-1}$ vs $1/\alpha$, the intercept gives the electron diffusion length, L_n .

The collection efficiency at long wavelengths (>830 nm,) where $1/\alpha \gg L_n$, is compared before (η) and after (η') heat treatment. It is assumed that the long wavelength light is absorbed uniformly in the sample, and the ratio of the two collection efficiencies is given by

$$\frac{\eta'}{\eta} = \frac{L_n + L_p + W_n + W_p}{L_n + W_p} \quad \text{C.3-4}$$

where L_p is the hole diffusion length in the n-region, W_n and W_p are the space-charge region widths in the two regions. W_p and $(W_n + W_p)$ are calculated from the capacitance of the sample.

FIGURE C.3-1: Log η vs $\sqrt{t}$ for n on p device heated at 120°C.

FIGURE C.3-2: Log η vs $\sqrt{T}$ for n-on-p device
heated at 100°C (ZP 199-1a)

FIGURE C.3-3: Log η vs $\sqrt{T}$ for n-on-p device
heated at 100°C (ZP 191-2)

Table C.3-I below gives the values of L_p , L_n , W_p , $(W_n + W_p)$ of these samples and

TABLE C.3-I

SAMPLE #	L_n (μm)	L_p (μm)	W_n (μm)	$(W_n + W_p)$ (μm)
ZP-199-1a	4.04	4.15	0.29	1.77 (100°C, 240 min)
ZP-199-1b	2.92	3.57	0.26	1.07 (125°C, 180 min)
ZP-191-2	5.8	8.76	0.35	1.43 (100°C, 180 min)

table C.3-II gives the calculated value of D at 100°C and 125°C.

TABLE C.3-II

SAMPLE #	N_p (cm^{-3})	D (cm^2/sec)	Temperature °C
ZP-199-1a	1.3×10^{16}	1.5×10^{-11}	100
ZP-191-2	9.5×10^{15}	2.4×10^{-11}	100
ZP-199-1b	4.5×10^{16}	5.0×10^{-11}	125

The spectral response method for the measurement of D was only useful for wafers with $N_p > 1 \times 10^{16} cm^{-3}$. In high resistivity wafers ($> 100 \Omega\text{-cm}$), a wide compensated region existed even for relatively short heat treatment times (< 1 hour). At short wavelengths, the carrier collection at the junction was assisted by the electric field in the n-layer as well as by diffusion. As a result, the effective diffusion length in the n-layer obtained by using equation C.3-4 was very long ($> 20 \mu m$). The series resistance of the devices increased ($> 100 \Omega\text{-cm}^2$) making the capacitance measurements for calculating W unreliable.

The diffusion coefficient may be dependent on the carrier concentration in the p-region and the crystal orientation. Laser scans of unheated devices or heavily p-doped Schottky devices show a fairly uniform response.

In contrast, laser scans of devices in which Mg was diffused in Zn_3P_2 show a relatively non-uniform response (Figure C.3-4) and exhibit features which appear to coincide with the grain structure. Therefore, we conclude that the spectral response method gives an average value of diffusion coefficient in the wafer.

C.4 Performance of p/n Homojunction Devices

The theoretical model for a Zn_3P_2 p-n homojunction device predicts a conversion efficiency, η , of 17%. The absorption coefficient of Zn_3P_2 is high, so that for high η , the n layer width must be $\leq 1 \mu\text{m}$. The calculated dependence of V_{oc} and J_{sc} given in section C.2 was compared to experiment by measuring J_{sc} , V_{oc} and the important diode parameters of transparent magnesium diodes as a function of time after heating at 75°C and 100°C . Figure C.4-1 gives the calculated values of junction depth x_j as a function of $(T)^{1/2}$ for various values of base concentration at 100°C . N_0 is assumed to be $1 \times 10^{17} \text{ cm}^{-3}$ with $D(100^\circ\text{C}) = 2.10^{-11} \text{ cm}^2/\text{sec}$. It is clear from Figure C.4-1 that in order to maintain a shallow junction, Zn_3P_2 wafers with $N_p \geq 5 \times 10^{16} \text{ cm}^{-3}$ should be chosen and the diffusion carried out at temperature $\leq 100^\circ\text{C}$. Table C.4-I gives the resistivity and carrier concentrations of the samples chosen for this experiment.

FIGURE C.3-4: Z-modulated laser scan of ZP-194-3 after heating for 1350 minutes at 100°C.

FIGURE C.4-1: Junction depth as a function of heating time calculated for various p-layer concentrations.

TABLE C.4-I

Sample #	p (Ω -cm)	N_D (cm^{-3}) from		
		$\mu = \frac{p}{20V-1} \text{cm}^2/\text{sec}$	$\frac{C(V=U)}{\phi_B = 0.8V}$	$\frac{d(1/c^2)}{dV}$
ZP-194-2	8.45	3.7×10^{16}	1.94×10^{16}	2.47×10^{16}
ZP-194-7	16.94	1.84×10^{16}	1.07×10^{17}	9.47×10^{16}
ZP-194-3	6.07	5.15×10^{16}	3.92×10^{16}	4.17×10^{16}
ZP-198-3a	7.5	4.17×10^{16}	1.22×10^{17}	1.1×10^{17}

Devices ZP-194-2 and ZP-194-7 were heated at 75°C while ZP-194-3 and ZP-198-3a were heated at 100°C. The essential light diode parameters for the devices are given in Table C.4-II to V. J_{SC} and V_{OC} of the devices are plotted as a function of $(T)^{1/2}$ (i.e., proportional to junction depth) in Figures C.4-2 to 5. In all cases the qualitative aspects of the theoretical predictions of section C.2 are confirmed. These are 1) an increase in J_{SC} for short diffusion time (shallow junction 75°C diffusion) followed by a gradual decrease and 2) an increase in V_{OC} as junction depth increases to a maximum value followed by a gradual decrease as J_{SC} falls off.

Although the qualitative features of the theoretical examination of section C.2 are confirmed, the open circuit voltage is much lower than these predications indicate. For example, the highest V_{OC} obtained is 0.575 volts for ZP-194-3 after 1350 minutes compared to a calculated value of $V_{OC} \geq 0.9$ volts as shown in Figure C.2-2. J_{SC} is in good quantitative agreement with theory when correction for probable optical losses are made.

FIGURE C.4-2: J_{sc} and V_{oc} vs $(\text{time})^{1/2}$ for device heated at 75°C.

FIGURE C.4-3: J_{sc} and V_{oc} vs $(time)^{1/2}$ of device heated at 75°C.

FIGURE C.4-4: J_{sc} and V_{oc} vs $(\text{time})^{\frac{1}{2}}$ for device heated at 100°C.

FIGURE C.4-5: J_{sc} and V_{oc} vs $(\text{time})^{1/2}$ for device heated at 100°C.

We believe the discrepancy may be accounted for on the basis of an incorrect assumption of the transport properties. The three assumptions made in calculation are 1) that $\mu_n = \mu_p = 25 \text{ cm}^2/\text{V}\cdot\text{sec}$, 2) $L_n = L_p$ and τ of the electron and hole are equal and 3) that the n-type dopant is fully ionized. If we use a value of $\mu_n = 1000 \text{ cm}^2/\text{V}\cdot\text{sec}$, which is plausible based on measurements of majority carrier mobility in n-type Cd_3P_2 and other II-V's, then J_{0d} and J_{0n} increase and V_{oc} decreases. It is clear that a refinement of the theoretical modeling depends on measurement of the transport properties of the n-type material in order to obtain the free electron concentration and donor levels, electron mobility and lifetime. These measurements will begin during the next quarter.

TABLE C.4-II
Diode Parameters of ZP-194-2 Heated at 75°C

Heating Time (min)	0	20	60	140	1250
J_{sc} (mA/cm ²)	15.0	15.09	15.09	14.61	11.26
V_{oc} (Volts)	0.438	0.457	0.465	0.508	0.563
FF	0.36	0.35	0.35	0.39	0.42
$\eta(\%)$	2.7	2.76	2.80	3.31	3.04
$R_s \times A(\Omega\text{-cm}^2)$	9.75	7.8	7.15	6.5	---
$R_{sm} \times A(\Omega\text{-cm}^2)$	812	812	810	650	500
(From $1/C^2 - V$) ϕ_B (eV)	1.0	1.43	1.85	2.29	2.1
$N_p(\text{cm}^{-3})$ from $\frac{d(1/C^2)}{dV}$	2.47×10^{16}	2.21×10^{16}	2.12×10^{16}	1.95×10^{16}	1.68×10^{15}
$N_p(\text{cm}^{-3})$ from $C(V=0)$	1.9×10^{16}	1.29×10^{16}	9.9×10^{15}	7.16×10^{15}	6.8×10^{14}
A	1.61 ± 7	2.01 ± 4	---	2.10 ± 7	1.97 ± 5
J_0 (Amp/cm ²)	5.04×10^{-7}	2.07×10^{-6}	---	1.5×10^{-6}	9.30×10^{-8}

TABLE C.4-III

Diode Parameters of ZP-194-7 Heated at 75°C

Heating Time (min)	0	30	90	210	450	1327
J_{sc} (mA/cm ²)	14.8	15.22	15.30	15.20	14.32	13.20
V_{oc} (Volts)	0.39	0.448	0.465	0.494	.513	.540
FF	0.43	0.45	0.45	0.46	0.47	0.46
$\eta(\%)$	2.84	3.50	3.66	3.95	3.94	3.76
$R_s \times A(\Omega\text{-cm}^2)$	5.0	5.0	5.0	5.0	5.5	6.5
$R_{sm} \times A(\Omega\text{-cm}^2)$	680	980	950	950	800	530
(From $1/C^2 - V$) $\phi_B(\text{eV})$	0.91	1.31	----	1.79	----	2.06
$N_p(\text{cm}^{-3})$ from $C(V = 0)$	9.47×10^{16}	3.89×10^{16}	----	3.59×10^{16}	----	1.55×10^{16}
$N_p(\text{cm}^{-3})$ from $(1/C^3)dV$	1.07×10^{17}	9.89×10^{16}	----	7.71×10^{16}	----	4.5×10^{16}
A	1.65	----	1.91	1.86	1.79	1.71
J_o (Amp/cm ²)	2.02×10^{-6}	----	1.20×10^{-6}	5.97×10^{-7}	2.13×10^{-7}	6.45×10^{-8}

TABLE C.4-IV

Diode Parameters of ZP-194-2 Heated at 100°C

Heating Time (min)	0	30	60	90	170	270	1350
J_{sc} (mA/cm ²)	15.2	14.46	13.23	12.61	11.20	9.51	5.23
V_{oc} (Volts)	0.42	0.493	0.520	0.537	0.559	0.574	0.575
FF	0.40	0.37	0.37	0.42	0.44	0.45	0.47
$\eta(\%)$	2.91	3.01	2.91	3.25	3.15	2.81	1.61
$R_s \times A(\Omega\text{-cm}^2)$	5.9	9.1	10.4	8.45	10.4	10.4	19.5
$R_{sm} \times A(\Omega\text{-cm}^2)$	810	800	650	325	325	440	1120
From $1/C^2 - V$ ϕ_B (eV)	1.05	2.62	3.1	2.98	2.6	2.95	3.03
N_p (cm ⁻³) From $\frac{d(1/C^2)}{dV}$	4.17×10^{16}	2.4×10^{16}	1.84×10^{16}	1.42×10^{16}	8.15×10^{15}	6.34×10^{15}	1.95×10^{16}
N_p (cm ⁻³) From $C(V=0)$	3.92×10^{16}	7.85×10^{15}	5.21×10^{15}	4.12×10^{15}	2.67×10^{15}	1.86×10^{15}	5.83×10^{14}
A	1.23		2.05		2.07	1.95	1.73
J_0 (Amp/cm ²)	3.36×10^{-8}		7.6×10^{-7}		3.33×10^{-7}	1.08×10^{-7}	1.30×10^{-8}

TABLE C.4-V

Diode Parameters of Sample ZP-198-3a Heated at 100°C

Heating Time (min)	0	30	60	120	210	2890
J_{SC} (mA/cm ²)	14.1	12.91	12.18	11.38	11.69	5.91
V_{OC} (Volts)	0.40	0.481	0.491	0.504	0.505	.442
FF	0.35	0.35	0.34	0.34	----	0.33
η (%)	2.19	2.48	2.32	2.22	----	0.98
$R_S \times A$ (Ω -cm ²)	4.22	5.85	5.32	7.5	----	11.70
$R_{Sn} \times A$ (Ω -cm ²)	650	----	610	490	520	---
From $1/C^2$ - V ϕ_B (eV)	0.90	1.19	1.17	1.28	1.74	1.13
N_p (from $C(V=0)$ (cm ⁻³)	1.1×10^{17}	5.27×10^{16}	4.57×10^{16}	3.79×10^{16}	3.35×10^{16}	1.52×10^{16}
N_p from $\frac{d(1/C^2)}{dV}$ (cm ⁻³)	1.22×10^{17}	7.77×10^{16}	6.73×10^{16}	6.1×10^{16}	6.95×10^{16}	2.35×10^{16}
A	1.64	2.08	----	----	2.01	1.66
J_0 (Amp/cm ²)	1.56×10^{-6}	----	1.39×10^{-6}	----	6.74×10^{-7}	2.16×10^{-7}

APPENDIX A

SUBSTRATE	COMMENTS
I. Metal films on mica	
1. Fe - 500 to 1000Å C - 500 to 1000Å	TMF Mg/Zn ₃ P ₂ Cells with $\eta \sim 2.75\%$
2. Fe - 500 to 1000Å Si - 100Å	TMF Mg/Zn ₃ P ₂ cells with $\eta \sim 2.7\%$
3. Fe - 1000Å W - 500Å C - 1000Å	$R_s \times A > 100 \Omega\text{-cm}^2$
4. Fe - 1000Å W - 800Å	$R_s \times A > 100 \Omega\text{-cm}^2$
5. Ni - 1000Å	Large whiskers on film
6. Ni - 1000Å C - 1000Å	
7. Ag - 500Å Fe - 500Å C - 1000Å	Poor Mg/Zn ₃ P ₂ diodes
8. Cu - 1000Å W - 650Å	Films crack and peel off
9. Au - 500Å W - 500Å	$R_s \times A > 1000 \Omega\text{-cm}^2$

APPENDIX A (Continued)

SUBSTRATE	COMMENTS
I. Metal films on mica	
10. W - 1000Å C - 700Å	Films peel off
11. Ag - 500Å	Film heavily Ag doped No Mg/Zn ₃ P ₂ diodes
II. Metal Substrates	
1. Silicon steel (3% Si) a) with Fe/C b) with Fe/Si c) with Al/C d) with W/C	TMF Mg/Zn ₃ P ₂ devices with $\eta \sim 2.5\%$ Low V_{oc} (~ 0.35 Volts) High R_s
2. Stainless Steel/Fe/C	Low V_{oc}
3. Al/Fe/C	$R_s \times A > 100 \Omega\text{-cm}^2$
4. Ion plated Al.	$R_s \times A > 100 \Omega\text{-cm}^2$